Magnetic and Structural Characterization of Ferrite-Ferroelectric Based Multiferroics Composites

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Abstract

In this study, the investigation of the magnetic and structural properties of the composite $(x)CoFe_2O_4$-$(1-x)SrTiO_3$, where x = 1.0, 0.6, 0.4, 0.2, synthesized via the solution combustion method have been done. The structural properties of the synthesized composites were characterized using X-ray diffraction (XRD) and analyzed through Rietveld refinement. Surface morphology was examined using scanning electron microscopy (SEM). XRD analysis confirmed a nanocrystalline ferrite phase with an average particle size of 63.44 nm. SEM micrographs revealed a reduction in grain size with a decreasing mole fraction of the ferroelectric phase. Magnetic characterization demonstrated a significant increase in coercivity with increasing $SrTiO_3$ content, while saturation magnetization decreased, attributable to the dilution of the magnetic phase. These findings indicate that the magnetic properties are strongly influenced by the $SrTiO_3$ concentration, with saturation magnetization inversely proportional to the $SrTiO_3$ content.

1.   Introduction

Recently ferroic materials have been widely used in multifunctional devices such as magnetic field sensors, actuators, transducers, four-state data storage devices, phase shifters [1-4], tunnable microwave filters [5] and electrical-driven magnetic antennae [6]. Magnetoelectric (ME) coupling in multiferroic material is the behaviour of a material to generate electric polarization when placed in a magnetic field or to generate magnetization when placed in an electric field [7-12]. Thus, the presence of coupled ferromagnetic and ferroelectric phases provides an extra degree of freedom for storage applications in which data could be written magnetically and read electrically and vice-versa [13].

Experimentally, the ME effect was first observed in single-phase Cr_2O_3 [14-15]. Several single-phase magnetoelectric materials have been investigated in the last few decades [16-18]. Single-phase magnetoelectric materials belong to the group of the perovskite transition metal oxides and include rare-earth manganites and ferrites such as $TbMnO_3$, $HoMn_2O_5$, $LuFe_2O_4$ and bismuth alloys $BiFeO_3$ [19-22] and $BiMnO_3$ [22-23] etc are rare and shows very low magnetoelectric coefficient (α) and low magnetization due to antiferromagnetic ordering at or above room temperature, which making them

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inadequate for potential device applications [24-25]. Interestingly, the ME composite multiferroics are often prepared by combining two different ferroic materials such as ferroelectric and ferromagnetic ordering may be a good substitute for single-phase ME multiferroic [2]. Many magnetoelectric composites have been prepared using strontium titanate $SrTiO_3$ (STO) as ferroelectric and cobalt ferrite $CoFe_2O_4$ (CFO) as piezomagnetic spinel ferrites. Ahmed et al. have studied the physical properties of novel $(1-y)Co_{0.8}Cu_{0.2}Fe_2O_4+(y)SrTiO3$ nanocomposite [26]. They found that saturation magnetisation (Ms) and Curie temperature (TC) decrease with increased SrTiO3 content. Kanamadi et al. have studied the magnetoelectric effect and complex impedance analysis of $(x)CoFe_2O_4+(1-x)Ba_{0.8}Sr_{0.2}TiO_3$ multiferroics [27]. Analysis of AC impedance data indicates a typical negative temperature coefficient of resistance. Also, The saturation magnetization was found to decrease with an increase in the phase fraction of BSTO in the composite. Pahuja et al. have studied structural, microstructural, dielectric, magnetic, ferroelectric and magnetoelectric properties of the $Ni_{0.8}Co_{0.2}Fe_2O_4$-$Ba_{0.95}Sr_{0.05}TiO_3$ multiferroic composites [28]. The composite samples show dielectric dispersion at low frequency due to the Maxwell–Wagner relaxation mechanism. The dielectric constant of the composite samples decreases with an increase in ferrite content. Grain and grain boundary resistance decreases with an increase in ferrite content. Sutar et al. have studied the magnetoelectric and magnetodielectric effect in $Ba_{1-x}Sr_xTiO_3$ and $Co_{0.9}Ni_{0.1}Fe_{2-x}Mn_xO_4$ composites [29]. The ME and MD properties results are understood in terms of the stress-induced variations in polarization and dielectric constant ε respectively. Pahuja et al. have studied the effect of rare earth substitution on the properties of $Ba_{0.95}Sr_{0.05}TiO_3$ ceramic and its multiferroic composite with $Ni_{0.8}Co_{0.2}Fe_2O_4$ [30]. Composite samples containing Dy, Gd and Sm substituted BST as ferroelectric phase possess lower values of remanent and saturation magnetizations in comparison to composite sample containing pure BST as ferroelectric phase (BSTC).

As per the best of our search, very little research on the structural and magnetic hysteresis of $(x)CoFe_2O_4$-$(1-x)SrTiO_3$ (CFO-STO) magnetoelectric multiferroics composites prepared by solution-combustion method has been reported earlier. In the present study, CFO was chosen as the ferrite phase due to its large magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, mechanical hardness and good chemical stability [31] and STO was chosen as the ferroelectric phase with good safety characteristics and relatively negligible irreversible capacity losses. Also, it shows low electronic conductivity which in turn provides large resistance [32].

2. **Experimental**

The composite with chemical composition $(x) CoFe_2O_4$-$(1-x)SrTiO_3$ (where x = 1.0, 0.6, 0.4, 0.2) was prepared by the solution combustion method. Precursor was prepared in ethylene glycol monomethyl ether $(C_3H_8O_2)$(Merck india >98%) from metal nitrates $Co(NO_3)_2.6H_2O$ (Merck india >99%), $Fe(NO_3)_3.9H_2O$ (Merck india >98%), $Sr(NO_3)$ (Merck india >99%) and $Ti(C_4H_9O)_4$ (Merck india >99%) with l-alanine $(C_3H_7NO_2)$ (Merck india >99%) was used as fuel. For each series, the 1:1 molar ratio of fuel and nitrates was taken. $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Sr(NO_3)$ and $Ti(C_4H_9O)_4$ were mixed in solvent $C_3H_8O_2$ one by one to form a clear solution in a beaker. The required amount of l-alanine was then mixed with the above solution and the mixture was stirred for 30 minutes. Then,

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the mixture was heated at 80 ° C and evaporated on the hot plate with stirring; until the auto-combustion started with the evaluation of gases as shown in Fig 1. The dark black colour ash was obtained after the complete combustion. The synthesized powder was then grinded and annealed at 800° C for 2 hours. Hereafter, the composites (x) $CoFe_2O_4$-(1-x)$SrTiO_3$ (where x=1.0, 0.6, 0.4, 0.2) are named as Pure, S4, S8, S10.

Fig.1 Sample preparation using auto-combustion

3. Characterization

The phase structures of the prepared samples were characterized by an X-ray diffractometer (XRD; XPERT PRO diffractometer) using Cu-K_α source with λ= 1.54Å. The microstructures of the prepared samples were analyzed using a scanning electron microscope (SEM). The ferromagnetic hysteresis loops of the prepared CFO-STO composite ceramics were characterized by a vibrating sample magnetometer (VSM; Lake Shore Model 7140, USA).

4. Result and discussion

4.1 X-ray diffraction

The X-ray diffraction (XRD) patterns of (x)$CoFe_2O_4$-(1-x)$SrTiO_3$ (x=1.0, 0.6, 0.4, 0.2) composite ceramic samples are shown in Fig 2.
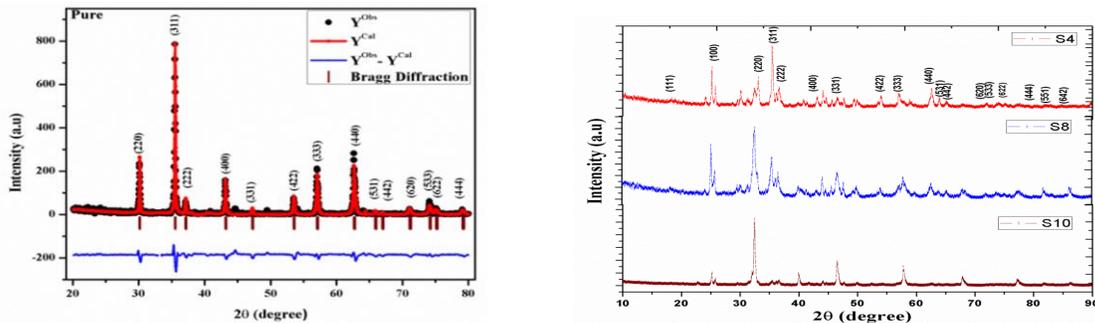

Fig 2. Rietveld Refinement of Pure and (XRD) diffraction patterns of (x)CoFe₂O₄-(1-x)SrTiO3 (x=1.0, 0.6,

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0.4, 0.2) composite ceramic.

The XRD shows two well-defined sets of different sets of diffraction peaks of the CFO and STO phases, which reveals that a single-phase cubic spinel structure for $CoFe_2O_4$ and cubic perovskite structure for $SrTiO_3$ have been synthesized. All the peaks are indexed using the standard powder diffraction data for $CoFe_2O_4$ and $SrTiO_3$.It can be seen that in the pure CFO phase, only a single α-Fe_2O_3 phase was observed at 2θ =33. Also, as expected, with the increase of STO mole percentage, the peak intensity corresponding to STO increases gradually while the peak intensity corresponding to CFO decreases. Particle size as calculated by Rietveld refinement is found to be 63.44nm. The Rietveld refinement lattice parameters of the pure sample of $CoFe_2O_4$ are reported in Table 1.

Table 1. Rietveld Refinement parameter of the Pure sample of $CoFe_2O_4$.

S.No.	hkl	Mult	HWFM	ETA/M	2Theta/TOF	I_{calc}	I_{obs}	Sigma	StrFactor^2	d-hkl
1	220	12	0.12323	0.57145	30.138	33.8	33.8	0.803	223.8718	2.96286
2	311	24	0.13147	0.6731	35.499	117.9	117.9	1.35	557.3979	2.52673
3	222	8	0.13423	0.70409	37.133	11.2	11.2	0.463	174.9013	2.41916
4	400	6	0.14511	0.81805	43.143	28	28	0.681	817.8754	2.09506
5	331	24	0.15317	0.89569	47.238	5.6	5.6	0.272	49.8714	1.92256
6	422	24	0.16659	1.0149	53.525	19	19	0.506	226.1518	1.71061
7	511	24	0.17471	1.08191	57.059	22.4	22.4	0.395	308.3157	1.61278
8	333	8	0.17471	1.08191	57.059	22.4	22.4	0.395	925.0657	1.61278
9	440	12	0.18849	1.18808	62.659	61.8	61.8	0.923	2093.7566	1.48143
10	531	48	0.19698	1.24922	65.883	4.9	4.9	0.29	46.7407	1.41652
11	442	24	0.19985	1.26925	66.94	2.7	2.7	0.168	53.2737	1.3967
12	620	24	0.21159	1.34792	71.088	9.3	9.3	0.344	205.1007	1.32503
13	533	24	0.22071	1.40563	74.132	14.6	14.6	0.426	350.3446	1.27797
14	622	24	0.22382	1.42467	75.136	7.9	7.9	0.289	194.2042	1.26337
15	444	8	0.23664	1.5	79.109	7.7	7.7	0.314	645.3356	1.20958

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Bragg R-factor: 4.64   RF-factor: 2.80

4.2 SEM analysis:

The SEM images of the composite series are shown in Fig. 3. For x = 1.0, 0.6 and 0.2 respectively indicating the presence of large randomly oriented grains. The density of all the sintered samples in the composite series was found to be close to 90% of the theoretical density for the $CoFe_2O_4$ composite. The surface morphology of all the ceramic composite as analysed from the SEM consists of well-crystallized grains, with relatively homogeneous grain distribution and an average grain size smaller than 100 nm, which is in good agreement with the XRD results. Also, the average grain size reduces as we decrease the mole percentage of the ferroelectric phase in the composite.
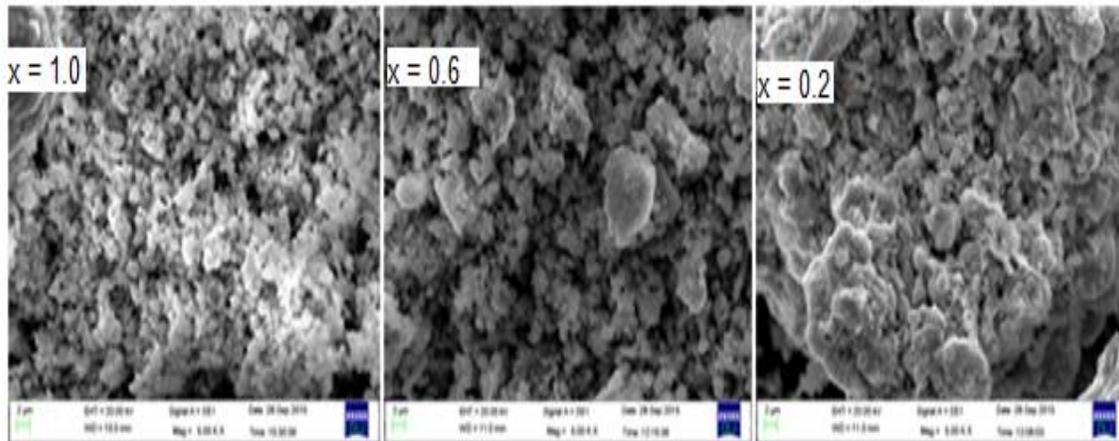

Fig.3. Scanning electron microscope (SEM) images of the (x)$CoFe_2O_4$-(1-x)$SrTiO_3$ composite ceramic.

4.3 Magnetic Study:

Fig 4 shows the room temperature M-H curve of all the samples at different concentrations. Magnetic properties of materials are characterized by a hysteresis loop, which gives the behaviour of a material when an external magnetic field is applied to the material. Magnetic properties of all composites were investigated using a Vibrating Sample Magnetometer with an applied field of −40 kOe to 40 kOe. As expected, the saturation magnetization (M_s) of the composites decreases with the increase of $SrTiO_3$ concentration. This is because the individual ferrite grains act as the centre of magnetization. The decrease in the magnetization values is mainly due to the dilution of the magnetic component [33]. The ferroelectric grains of $SrTiO_3$ create a shield that splits magnetic grains of the ferromagnetic phase leading to the weakening of the exchange coupling between them. Consequently, the magnetization decreases with the increases in the $SrTiO_3$ concentration.

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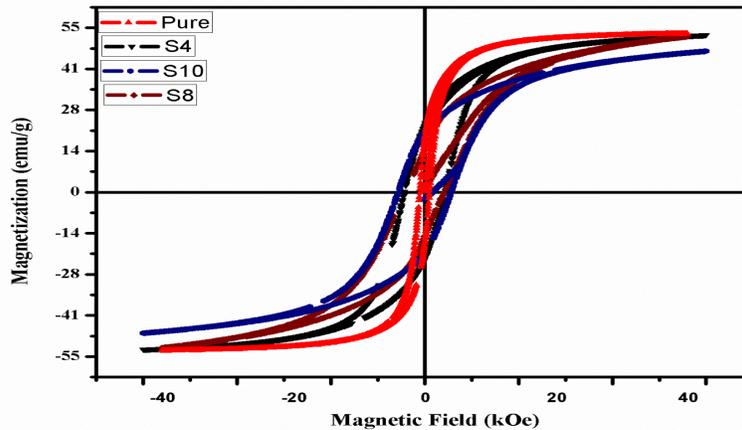
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Fig4. M-H Loops of (x)CoFe$_2$O$_4$-(1-x)SrTiO$_3$ (x=1.0, 0.6, 0.4, 0.2) composite ceramic.

5. Discussion and conclusions

We have successfully synthesized and characterized the (x)CoFe$_2$O$_4$-(1-x)SrTiO$_3$ (where x=1.0, 0.6, 0.4, 0.2) spinel- perovskite magnetoelectric composite ceramic by solution-combustion method. The Rietveld refinement of X-ray results for the obtained composite showed a nanocrystalline ferrite phase with average values of particle size 63.44nm. The SEM images show that the grain size reduces as we decrease the mole percentage of the ferroelectric phase. The magnetic studies reveal that saturation magnetization decreases with increasing SrTiO$_3$ content due to the dilution of the magnetic component.

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